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ZEOLITE CATALYSIS - TECHNOLOGY

Heinz Heinemann

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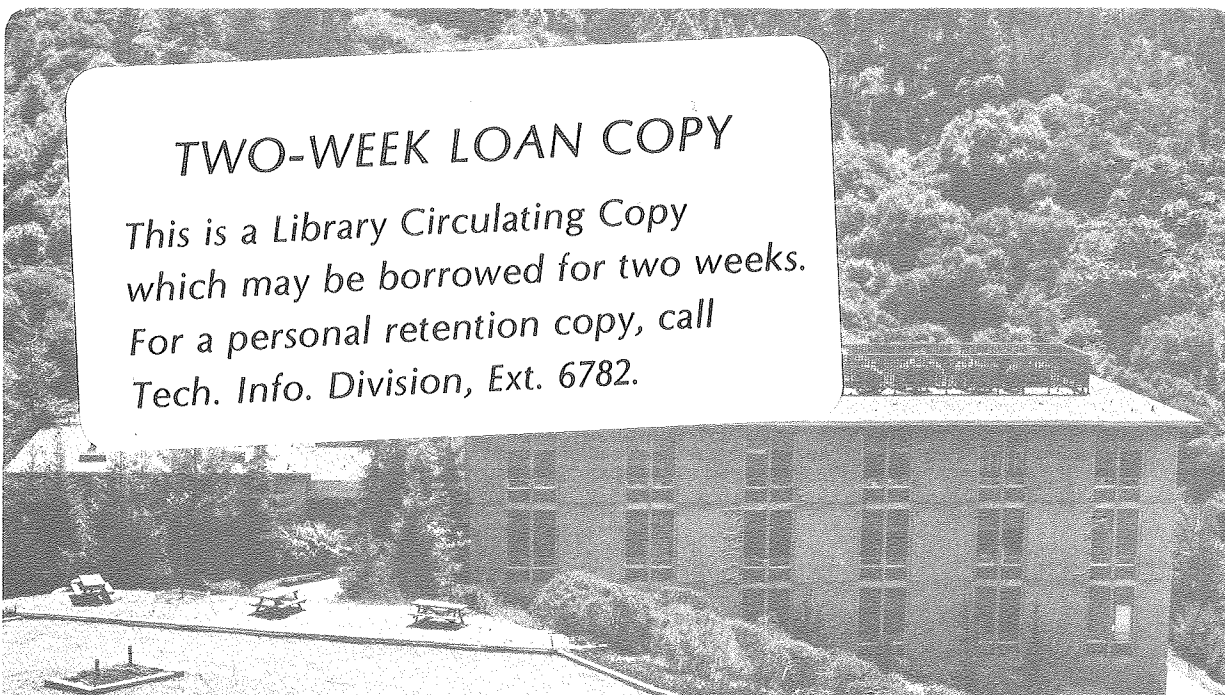
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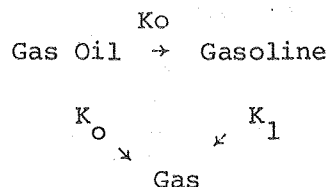
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Zeolites have been used as catalysts in industry since the early nineteen sixties. The great majority of commercial applications employ one of three zeolite types: zeolite Y; Mordenite; ZSM-5. By far the largest use of zeolites is in catalytic cracking, and to a lesser extent in hydrocracking. Table 1 presents some data showing the commercial importance of this field.

(1) The data are for U. S. refineries only and must be multiplied by a factor to arrive at world-wide use. Better than 90% of free-world cracking units now use zeolite catalysts. For many years it had been assumed that crystalline aluminosilicates with their uniform pore structure would make inferior catalysts to amorphous silica-alumina with a rather wide pore size distribution. The tremendous acid activity of hydrogen zeolites also was not recognized. Rabo and coworkers(2) showed at the 2nd International Congress on Catalysis that hydrogen exchanged faujasites possessed good isomerization ability, but commercial application in catalytic cracking became feasible only after Plank and Rosinsky at Socony-Mobil Oil Company succeeded in stabilizing zeolite Y against steam and heat sintering by exchange with rare earth ions and by separating zeolite crystallites by incorporating them into a silica-alumina matrix, which provided a heat reservoir along with some synergistic cracking effects. Modern cracking catalysts comprise 10-40% rare earth exchanged H-Y zeolite dispersed in a matrix of silica-alumina, semi-synthetic clay or natural clay.

In general, use of H-Y catalysts has resulted in much greater selectivity to gasoline, with lower gas and coke yields, as well as improved octane number. The effect of greater selectivity is dramatically shown in Fig. 1. U. S. cracking capacity actually declined for two years after introduction of zeolite cracking catalysts in 1964 and then resumed its increase at a lower slope while demand for gasoline continued to increase at a steady rate. Much more gasoline could be produced from a barrel of gas oil than with amorphous silica-alumina catalysts (Table 2). The improvement in octane number is due to a higher aromatic and isoparaffin content as shown in Table 3 (3). Weisz (3) has suggested that the interrelated differences in yield and composition are due to improved hydrogen transfer ability over the zeolite. A model



has been proposed (4). The secondary cracking of gasoline to gas,  $K_1$  is inhibited over the zeolite. One can describe this as due to the rapid formation of paraffins and aromatics from olefins and naphthenes. The former are much more refractory and tend to resist secondary cracking. Rabo, Bezman and Poutsma state (5) that HY "favors bimolecular (hydrogen transfer) steps over the monomolecular reaction (fragmentation) steps. Zeolites concentrate hydrocarbon reactants to a larger extent within the zeolite crystal than other catalysts." Over the years and since the first introduction of zeolites to catalytic cracking many catalyst improvements have been made, each leading to better gasoline yields (7). While the first use of zeolite cracking catalysts was in T.C.C. units, employing bead catalyst, fluid bed catalysts were soon introduced. Diffusional constraints during regeneration

which limited the size of moving bed units were not encountered with the small mesh fluid bed catalyst. However, a residual coke level of 0.5-1.0% was normal even in fluid bed units after regeneration. Yet complete burn-off of coke can greatly increase catalyst activity as shown in Fig. 2. (8). In 1977, Mobil Oil Company introduced zeolite cracking catalysts, which contained, in addition to the stabilized Y component, 0.1-50 ppm of platinum. The metal acted as a combustion catalyst during regeneration and did not appreciably increase hydrogen production by dehydrogenation during reaction. It serves not only to reduce residual coke on the catalyst but also to promote oxidation of CO to CO<sub>2</sub>, an exothermic reaction providing better heat recovery and pollution control (Table 4). It must be assumed that most of the very small amount of platinum on the catalyst is located on the matrix material rather than the zeolite crystallites. The drop in residual coke must therefore be due either to higher level temperatures radiating from the matrix to the zeolite or to a higher residual coke concentration on the matrix than on the zeolite.

It has been mentioned earlier that Y-type zeolites also have found large-scale application in hydrocracking (9). Hydrocracking is catalytic cracking in the presence of hydrogen with a dual functional catalyst possessing both cracking and hydrogenation-dehydrogenation properties. Large pore zeolites, such as Y and particularly ultra stable Y, are used in conjunction with either platinum or palladium in relatively small amounts or nickel, tungsten or molybdenum oxides in larger amounts. The Unicracking process developed by Union Oil Company and Exxon employs a two or three reactor system and can handle a wide variety of charge stocks, including heavy residual materials. (10; 11). Other processes have been developed by Chevron and Amoco.

The first reactor, which in some cases contains a non-zeolite based Ni-W catalyst only, serves as a hydrogenation zone to convert nitrogen and sulfur compounds to ammonia and hydrogen sulfide, respectively. These are less poisonous to the hydrocracking catalyst in the following reactor(s) than the original heterocyclics. In another variant, ammonia and  $H_2S$  are removed from the hydrogen before going to the hydrocracking reactor.

Hydrocracking produces a broad range of distillate fuels and may soon find application in the conversion of shale oils and coal liquids. The catalysts have very long life and can be regenerated by conventional means.

Another dual functional use of zeolite containing catalysts is the isomerization of  $C_5$  and  $C_6$  paraffin hydrocarbons. Shell Oil Company's "Hysomer" process employs a large pore mordenite containing small amounts of palladium. (12) While the catalysts are similar to hydrocracking catalysts, they are employed at mild enough conditions to minimize cracking and optimize isomerization, which at equilibrium can produce an increase of as much as 12 octane numbers (5).

In the early nineteen-sixties when catalytic cracking became prevalent, P. B. Weisz and his coworkers (13) discovered catalytic shape selectivity. They stipulated and demonstrated that diffusional constraints restricted the entry of molecules above certain dimensions into the pores of intermediate pore size zeolites. A number of processes have been developed and commercialized, mostly by Mobil Oil Company, using shape selective zeolites, such as erionite ( $\sim 5\text{\AA}$  pore size), ZSM-5 ( $6-7\text{\AA}$  pore size) and in one case mordenite.

Shape selective hydrocracking is the underlying principle of four processes. The earliest of these, "Selectoforming" (14) uses an erionite containing a small amount of a hydrogenation component such as nickel to selectively hydrocrack n-paraffins out of a naphtha reformat. Since n-paraffins are the lowest octane number component of reformates, this leads

to an octane improvement with relatively low volume losses. The major cracked component is propane and the process has been suggested also as a producer of LPG. Fig. 3 shows that the combination of reforming and Selectoforming can result in high octane number product at yields which are not obtainable with reforming alone, at least not without very rapid catalyst deactivation.

The Selectoforming process was superseded by the M-forming process used in Mobil's Wilhelmshaven (Germany) refinery. In M-forming the erionite zeolite is replaced by zeolite ZSM-5, which has a larger pore opening (6-7Å) and can admit singly branched paraffins as well as simple aromatics. This permits the removal by hydrocracking from reformate of the second lowest octane number component, singly branched paraffins. In this case, however, part of the olefinic component of the cracked product is alkylated onto aromatics, such as benzene and toluene. The resultant alkylaromatics contribute to octane number and reduce the loss of cracked products to gas, thus increasing liquid yield (15). In Table 5 (16) it is shown that the reactivity of olefinic fragments is such that essentially no olefinic cracked fragments are found in the product. Fig. 4 (16) demonstrates the remarkable efficiency with which ZSM-5 can produce alkylaromatics from n-paraffin/benzene mixtures for a series of  $C_5$ - $C_{16}$  n-paraffins.

Two other shape selective hydrocracking processes are designed to selectively remove waxy materials from distillate fuels and lubricating oils. Thus far commercial use has been made of both, the British Petroleum Company's (B.P.) process (17) and the Mobil Oil Company process (18; 19; 20) for lowering the pour point of distillate fuels and extending the usable end point of these fuels, thus increasing the yield of diesel, turbine, and No. 2 heating oil obtainable from a barrel of crude. The B.P. process employs

a metal loaded (probably palladium) tubular pore zeolite such as mordenite, while the Mobil process uses ZSM-5 zeolite. Hydrogen pressure requirements are higher for the B.P. process, since mordenite has more coking tendency than ZSM-5. Fig. 5 shows the effective removal of long chain n-paraffins in the Mobil process (18) and Table 6 (18) demonstrates the remarkable pour point reduction.

Zeolite ZSM-5 is unique among zeolites in the number of reactions for which it has found large scale application. In addition to those previously mentioned, xylene isomerization is prominent. There are two xylene isomerization processes with ZSM-5, one for operation at elevated hydrogen pressure and one for operation at near atmospheric pressure in the absence of hydrogen. (21). The former has found application in better than 2/3 of the world's xylene isomerization units, requiring essentially no equipment change from the previously used platinum-alumina catalyst process. A major advantage of the zeolite catalyst is that it disproportionates ethylbenzene in the feed to toluene and trimethylbenzenes. Both of these compounds are easily separated from the product. By contrast, the  $\text{Pt-Al}_2\text{O}_3$  catalyst isomerizes a small fraction of the ethylbenzene only and requires fractionation to avoid ethylbenzene build-up in the recycle. This is a complex separation because of the close boiling points of ethylbenzene and paraxylene. ZSM-5 disproportionates ethylbenzene, but in contrast to large pore zeolites causes very little xylene disproportionation as shown in Fig. 6 (21). Different mechanisms must prevail for the xylene isomerization over a dual functional catalyst and over an acidic zeolite.

Alkylation of aromatics with olefins has been discussed earlier for the M-forming process. It is also being used to produce ethylbenzene from benzene and ethylene in the Badger-Mobil process over ZSM-5. This process avoids the environmental and corrosion problems connected with Friedel-Crafts catalysts. Operating conditions are sufficiently different from the xylene

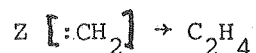


isomerization process to avoid disproportionation (22). The high temperature reaction provides efficient heat recovery. Catalyst regeneration is relatively infrequently required (2-3 weeks) in contrast to the rapid deactivation of large pore zeolites for this reaction.

Finally, a toluene disproportionation process has been operated with ZSM-5 to give benzene and xylenes (21). While xylene disproportionation is minimal in the xylene isomerization process, the disproportionation of toluene proceeds well at about 200°C higher temperature where steric constraints are greatly decreased.

Perhaps the most talked about process catalyzed by zeolite ZSM-5 is the conversion of methanol to gasoline, which has been described in a considerable number of papers (23-26). While there are as yet no commercial units operating, plans have been announced to build a 15,000 bbl/day plant in New Zealand. Methanol, which may be derived from either natural gas or coal, is dehydrated to dimethylether, which in turn is dehydrated to olefins. The olefins are polymerized to aromatics and hydrogen transfer from this polymerization saturates other olefins to paraffins. The paraffins are largely branched chain paraffins (Fig. 7), no products larger than  $C_{11}$  are produced because of the shape selective constraints. Methane production is less than 1%. The major product is gasoline of 94-96 octane number with a small amount of  $C_3$  and  $C_4$  hydrocarbons as a by-product. The latter can be alkylated to provide additional high octane gasoline. The reaction is highly exothermic and can be carried out in two reactors to split the heat load. In the first an equilibrium mixture of methanol and dimethylether is established over activated alumina. The effluent is fed to a second reactor which can be either a fixed bed reactor with gas recycle or a fluid bed reactor using the zeolite catalyst. Both configurations have been successfully tested in a 3-4 barrel/day pilot plant.

Two mechanisms have been proposed for the conversion of dimethylether. Chang and Silvestri (24) favor a carbene mechanism. Methylene diradical, once formed, can dimerize



or interact with methanol and dimethylether via  $\text{Sp}^3$  C-H insertion. Kaeding and Butler (27) propose a carbonium ion mechanism as shown in Fig. 8. Ethylene is the primary product of both mechanisms. It is found in smaller quantities in the product than propylene and other hydrocarbons, probably because of rapid secondary reactions, such as the alkylation of olefin with methanol to give the next higher olefin. (27).

Work has been done in several locations on the direct conversion of carbon monoxide and hydrogen to hydrocarbons over zeolite ZSM-5 either impregnated or mixed with Fischer-Tropsch metals or metal oxides. (28-29). While results have been interesting and promising, particularly in making high octane gasoline, development work is still lacking and there are no commercial applications in sight for the nearer future.

Another area of great interest has been the production of chemical building blocks, such as olefins and aromatics from coal derived methanol (28). Again work with various zeolites is in progress, but no processes are available today.

All of this, however, indicates that the rapid development of zeolite catalysis beginning about 1960 which has led to large scale applications and use of zeolites is accelerating and that we even expect new process technology in the area over the next decade or so.

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TABLE 1

Use of zeolite cracking catalysts in the U.S.A. in 1978

	<u>Catalytic Cracking</u>	<u>Catalytic Hydrocracking</u>
Capacity, bbl/day	5,000,000	900,000
metric tons/day	635,000	114,000
Catalyst Sales		
million lbs/yr	286	2
Catalyst value	143	20
\$/year in million		

From: D. P. Burke, Chemical Week 1979, 124 (13), 42

TABLE 2

Yield of Products from Cycle Stocks

	Amorphous <u>Si Al<sub>2</sub>O<sub>3</sub></u>	H-Y <u>Catalyst</u>	<u>Difference</u>
Conversion Vol %	35.6	35.6	-
C <sub>5</sub> + Gasoline, Vol %	22.1	29.2	+ 7.1
C <sub>4</sub> Vol %	8.7	6.2	- 2.5
Dry Gas Wt. %	5.2	3.5	- 1.8
Coke, Wt. %	4.3	1.4	- 2.9

From: Eastwood et al. (6)

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TABLE 3

Gasoline Composition from Cracking with  
amorphous and crystalline alumino silicates

	Amorphous $\text{SiO}_2\text{-Al}_2\text{O}_3$	H-Y Catalyst	Difference
Paraffins, %	13	23	+ 10
Olefins	17	5	- 12
Naphthenes	41	23	- 18
Aromatics	29	49	+ 20

From: Eastwood et al (6)

Table 4

Relative CO oxidation  
Activities of catalysts

Catalyst	Relative CO Oxidation Activity
Standard Catalysts CO Oxidation Type	1
Partial Combustion Catalysts	40
Complete Combustion Catalysts	150

From: *Rheume*, et al. (8)



Table 5

1/1 Weight Blend n-Octantane/Benzene over ZSM-5  
600°F, 700 psig, 4 LHSV

	Products, Wt %
Methane + Ethane	< 0.1
Propylene	< 0.1
Propane	7.3
Butanes	10.7
Pentanes	5.7
C <sub>6</sub> + C <sub>7</sub> Paraffins	2.4
Octane	6.4
Benzene	24.7
Toluene	0.5
C <sub>8</sub> Alkylbenzenes	1.3
Iso-propylbenzene	8.5
n-Propylbenzene	11.2
Other C <sub>9</sub> Alkylbenzenes	0.5
n + sec-Butylbenzene	7.1
Tert-Butylbenzene	1.9
Other C <sub>10</sub> Alkylbenzenes	1.7
C <sub>11</sub> + Alkylbenzenes	10.1
	100.0

From: Garwood et al. (16)

Table 6

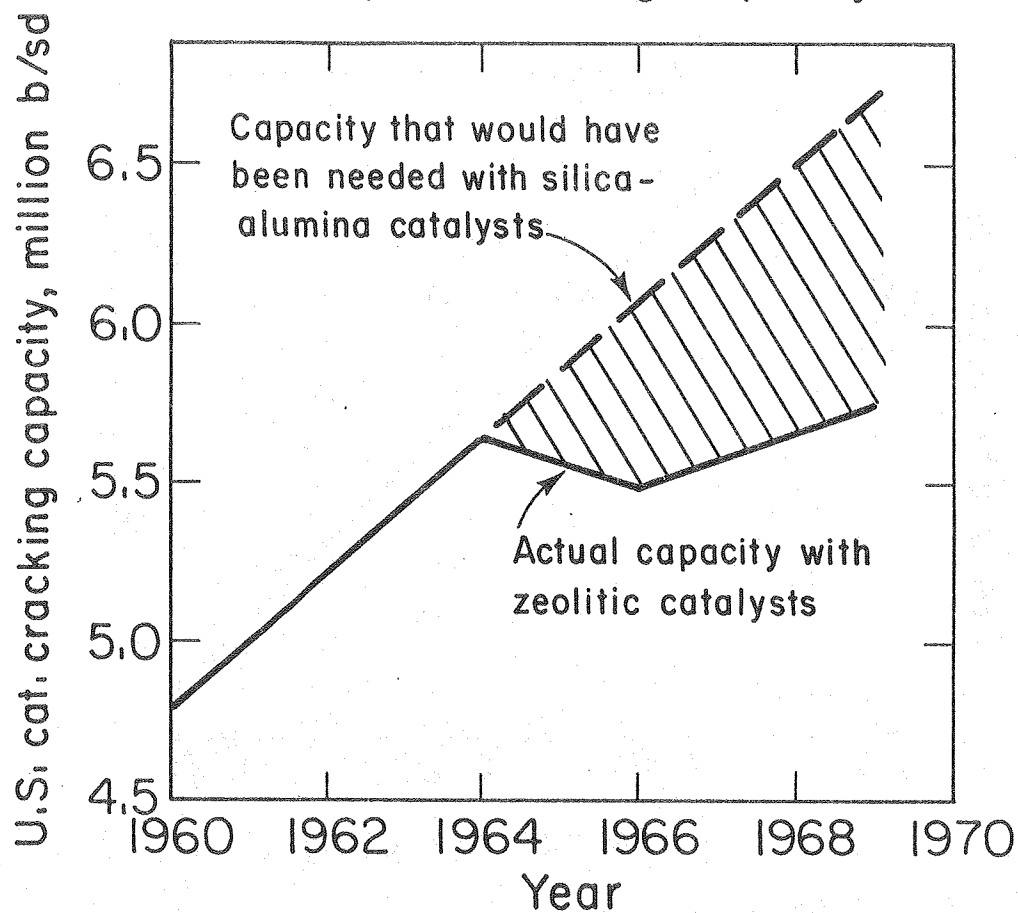
Properties of various oils before and after  
Hydrodewaxing with 2SH-5

Fraction	Virgin heavy gas oil	MMDW processed heavy gas oil
TBP cut, °F.	650-750	650-750
Yield on crude, vol %	7.5	6.3
Properties		
Gravity, °API	27.8	25.4
Pour point, °F.	60	-10
Cloud point, °F.	66	+ 22
Sulfur, wt %	2.3	2.5
Diesel index	46	38
ASTM dist., °F.		
10 vol %	658	653
50 vol %	685	682
90 vol %	732	731

From: *Chen, Goring, Ireland and Stein (18)*

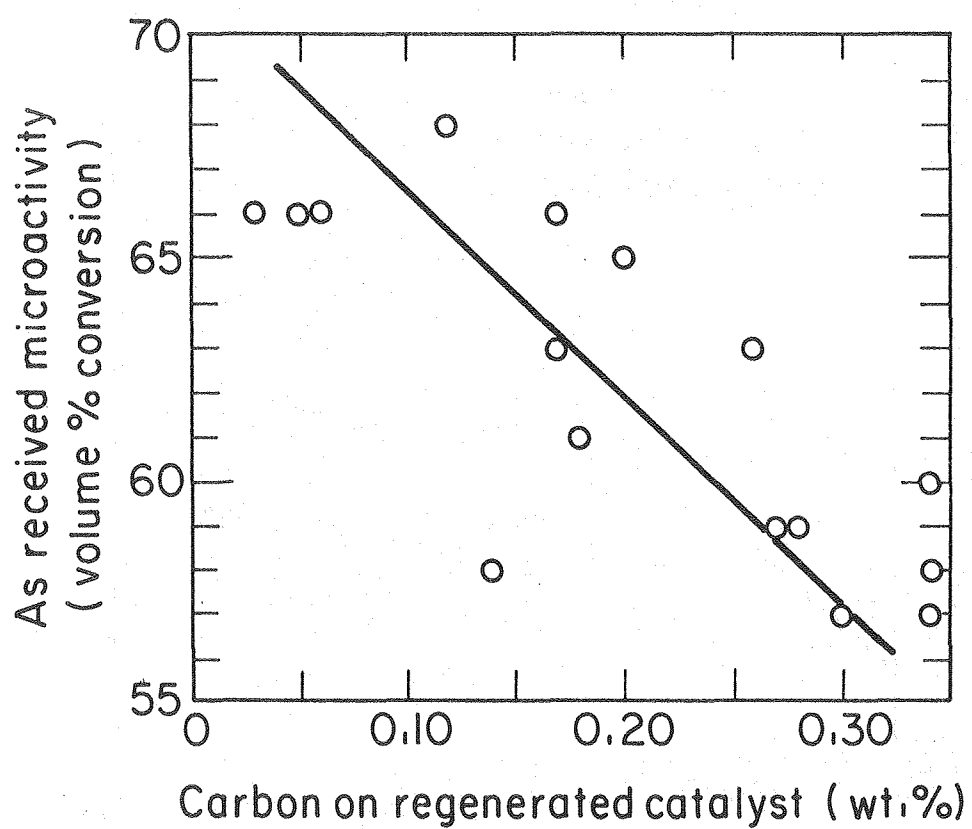
FIGURE 1

## Effect of Zeolitic Catalysts on Catalytic Cracking Capacity



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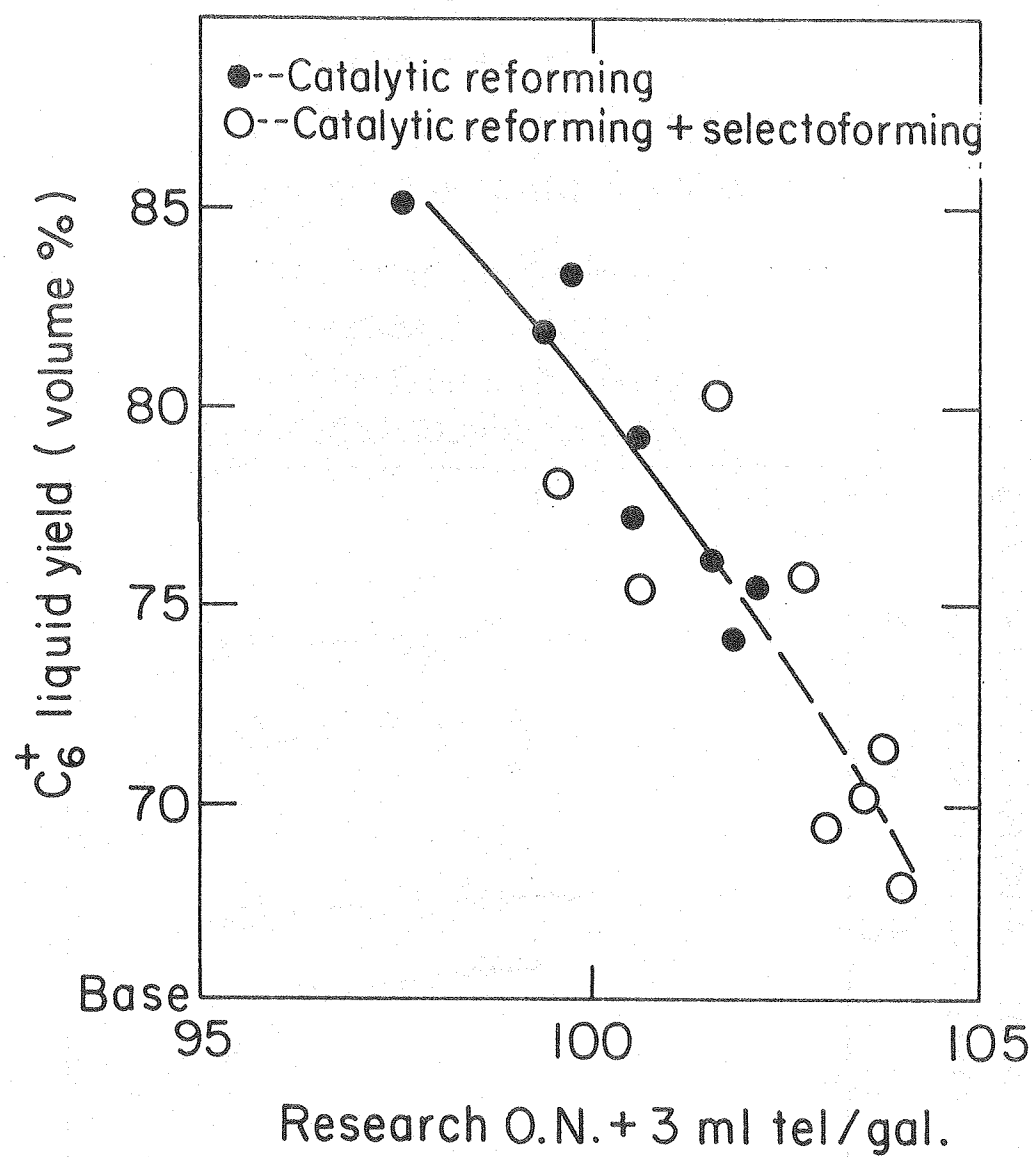
FIGURE 2



From: Rheume, et al.

XBL 805-1065

FIGURE 3



XBL 805-1066

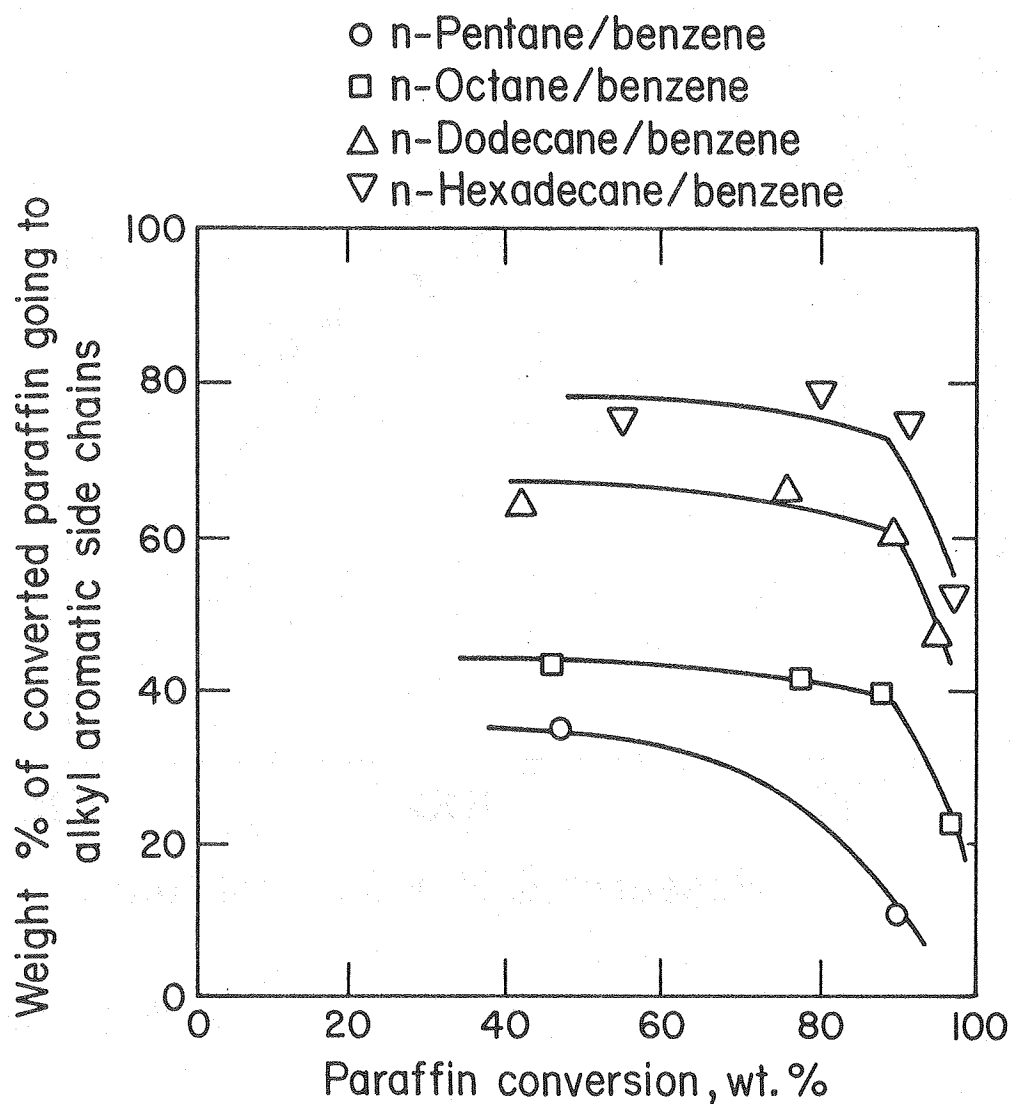
FIGURE 4

Conversion of n-paraffins  
to alkyl aromatic side chains

ZSM-5 catalyst

600 °F , 700 psig, 1/1 wt. blend

Severity controlled by space velocity



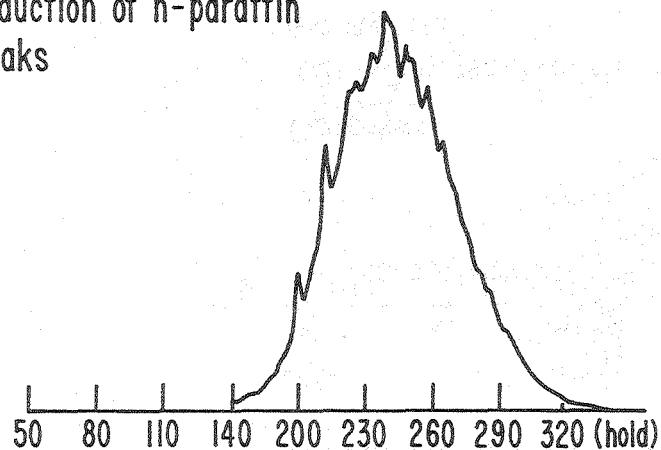
From: Garwood, et al. (16).

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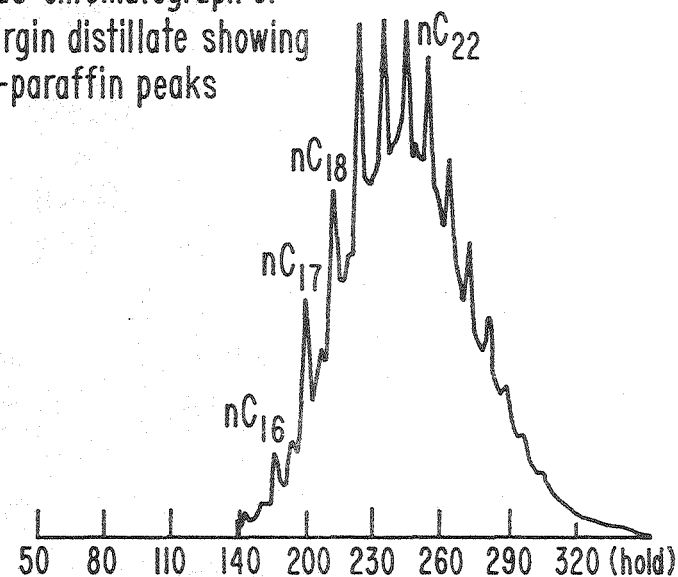
FIGURE 5

### Chromatograph reveals reductions in n-paraffin peaks over ZSM-5

Gas chromatograph of  
distillate after processing  
over MDDW catalyst showing  
reduction of n-paraffin  
peaks



Gas chromatograph of  
virgin distillate showing  
n-paraffin peaks



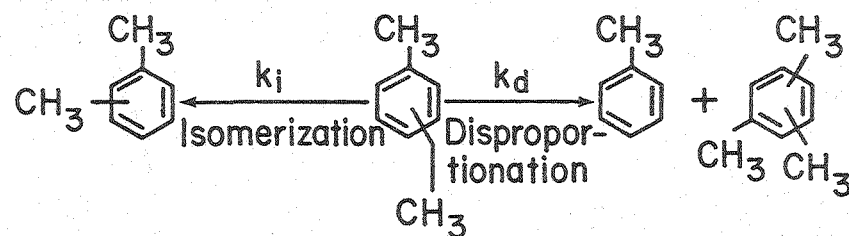
Programmed temperature, °C

*From: Chen, Gorrington, Ireland and Stein (18).*

XBL 805-1074

FIGURE 6

# XYLENE ISOMERIZATION/DISPROPORTIONATION



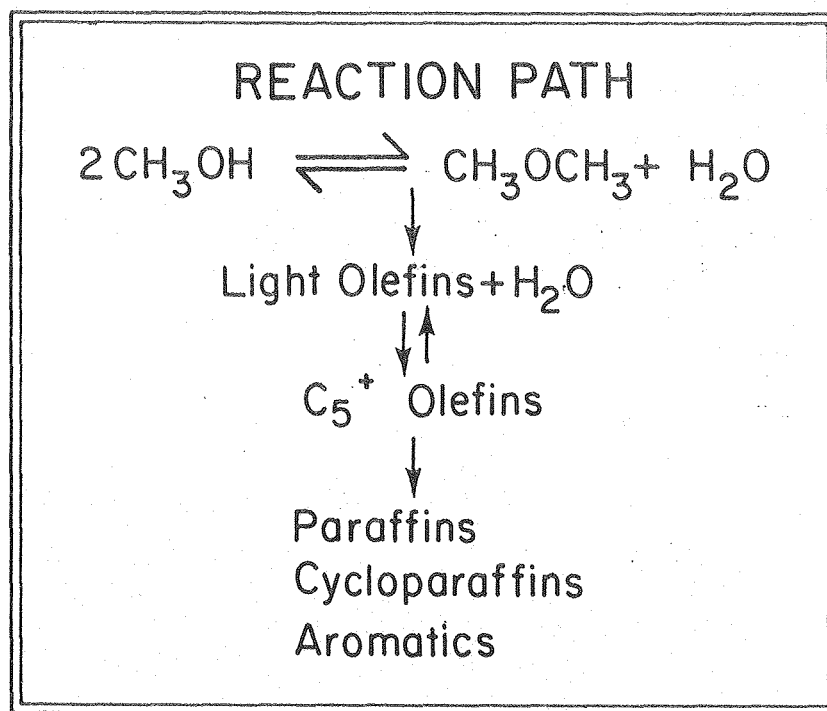
Catalyst	$k_i/k_d$
ZSM-5 class zeolite	1000
Mordenite	70
Faujasite	10-20

*From Meisel, McCullough, Lechfahler and Weisz (21).*

XBL805-1076



FIGURE 7

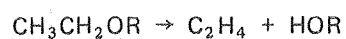
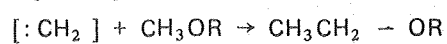
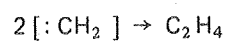


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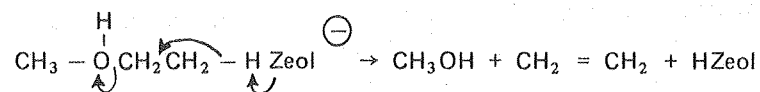
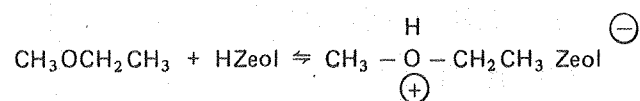
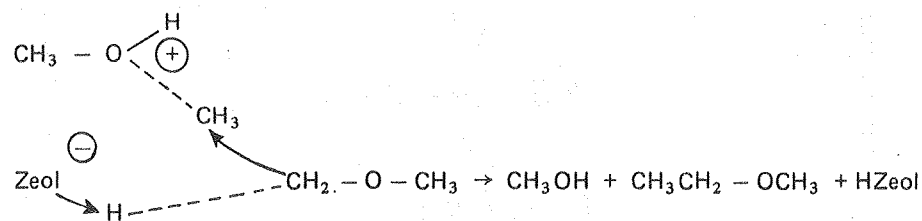
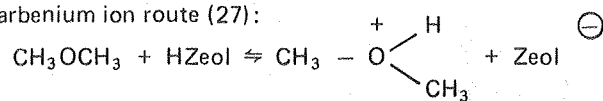
Fig. 8

Methanol Conversion Mechanisms

1) Carbene route: <sup>(24)</sup>



2) Carbenium ion route (27):



Net

